

From the fact that T'_{AB} is equal for molecules of the same chemical type two conclusions follow. Let each molecule of A attract a molecule of B by a force which is a function only of the distance which separates them, the density term in the Laplacian theory then becomes the reciprocal of the molecular volume and, following the usual notation,

$$T'_{AB} = \frac{\pi}{v_A v_B} \int_0^\infty z \psi_{AB}(z) dz,$$

v_A , v_B , being respectively the molecular volumes, and z the axis normal to the interface. Then on Young's hypothesis, that molecular attraction is a force which is of constant value over the range a , we have for two similar chemical substances, for which therefore T'_{AB} is the same, $a_1/a_2 = v_A'/v_A''$. That is to say, the range would be proportional to the molecular volume.

The alternative assumption, that the attractive force of a molecule of A for one of B falls off according to some power of the distance which separates them, yields the result that for similar chemical substances, since T'_{AB} is equal, the molecular volumes vary inversely with this power. Thus, if the attractive force $\phi(f)$ be put $= e^{-\beta f}$ then $v_A'/v_A'' = \beta_1^5/\beta_2^5$.

The Tension of Composite Fluid Surfaces.—No. II.

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With the figures in Table III of the preceding paper (p. 311) as a guide the problem of the spreading of one fluid over the surface of another may be approached with some sense of security. In an earlier paper* the equation of a composite surface was found to be $T_s = T_A + T_{AB} - Kg$ when T_s is the tension of the composite surface, and Kg a term depending upon gravity. Putting $Kg = 0$, it is seen that spreading will occur only when $T_s > T_A + T_{AB}$, and, at the limit, $T_s = T_B$ that is to the tension of pure water in the experiments under consideration.

Taking $T_B = 74$, the tension of pure water, we have from the last paper

Table I.

	T_A .		T_{AB} .	
Cyclohexane	24·21	+	55·15	= 79·36
Octane	20·63		52·96	73·59
Oil "C"	30·12		61·35	91·47
Carbon disulphide.....	30·88		56·15	87·03
Carbon tetrachloride.....	24·51		50·18	74·69

* 'Roy. Soc. Proc.' 1912, A, vol. 86, p. 610.

That is to say a drop of any of these saturated substances should not spread upon a surface of pure water except octane, and in actual fact none of them do spread, except octane, a drop of which slowly expands on water to form a very thin plate. In the case of all the other substances examined the quantity $(T_A + T_{AB}) < T_B$, and they all flash over a water surface in characteristic fashion.

The word "spreading" here refers strictly to the expansion of a lens of A over a clean surface of B due to the tension of B being greater than the sum of the tensions of the upper and lower surfaces of the lens. The vapour of A will condense on to the surface of B since $T_{AB} < T_B$. At the edge of a lens there is therefore a condensation of vapour of A on to the water, and the sheet of lowered tension so produced is pulled outwards away from the lens by the higher tension of the water surface. The sheet will also be pulled inwards to the lens, a quantity of the vapour of A so finding its way back into the lens. When the saturated substance has a high vapour pressure, such as *e.g.* cyclohexane, the presence of unstable sheets of condensed vapour about each lens is easily detected and readily explains the interesting attractions and repulsions of lenses for each other. When undisturbed a pair of lenses will often continue alternately to attract and repel one another, producing a quite regular pulsation.* The movements cease when the space above the surface is saturated with the vapour of A.

When the vapour tension of A is practically zero a lens shows no trace of spreading of any kind. This is the case with oil "C," which boils somewhere about 400° . For the sum of the tensions of the upper and lower surfaces of a lens of this oil we have $T_A + T_{AB} = 30.12 + 61.35 = 91.47$. It is obviously impossible for the tension of water (74) to pull such a lens out into a sheet.

When the fluid A is a pure chemical substance, or when it is composed of substances having identical influence upon the tension, the phenomena of spreading are always of the simplest. The first added fluid forms a continuous sheet on the surface of the water (B), which may be thickened until spreading ceases, when the excess remains as a single lens. I have met no exception to the rule that, when pure A spreads on water, the equilibrium state is a single lens in tensile balance with a uniform composite sheet of A spread evenly on B. This follows from experiment and also from a consideration of vapour pressures; for let the space above be enclosed, and

* Cantor ('Wied. Annal.,' 1895, vol. 56, p. 492) is wrong in his conclusion that the vapours of fluids which do not "wet" the surface of water will not condense on to the surface. The saturated vapours of the substances mentioned in Table I will condense on to tap water at the same temperature, as a dew of fine lenses, though in the case of carbon bisulphide owing to the high value of $T_A + T_{AB}$ the dew forms only with difficulty.

let a number of lenses of different horizontal diameters be formed. Lenses of greater curvature will lose vapour, and lenses of less curvature will condense it until a single lens is formed. A number of lenses of precisely the same curvature could co-exist, but the equilibrium would probably always be unstable. The condition of equilibrium therefore is twofold, (1) that the lens and the plane surface are in tensile equilibrium according to the equation $T = T_A + T_{AB} - Kg$, and (2) that the vapour tension of the lens and of the plane surface shall be the same.

When a large lens of a fluid whose vapour pressure is negligible is placed on water if it is capable of spreading the lens is at once extended to form an irregular sheet, which then proceeds to contract to one or more lenses which are in tensile equilibrium with a composite surface. Equilibrium is reached quickly when salts are present in the water and slowly when the water is of low conductivity. Taking, for instance, ricinolic acid as an example, equilibrium is reached with tap water in 20 seconds, and with distilled water only after perhaps 20 minutes. When distilled water is used there appears to be a large tangential viscosity which impedes contraction of the excess oil. As I have already pointed out* the film is at a different electrical potential to the underlying water, and the tangential viscosity may be due to the low conductivity of distilled water delaying the dissipation of electrical energy. Whatever be the true explanation the contrast is remarkable. When distilled water is used the tangential viscosity is so great as to allow the sheet of acid to develop wrinkles and folds as though it were a solid.

What we may picture as happening in all cases is that since $T_B > T_A + T_{AB}$ the lens is at once pulled out to form a sheet. From the visible edge of the sheet fluid is spreading on to the surface of B, at first rapidly, then more slowly, the flow being impeded by the viscosity of the film and possibly by other causes. As a consequence of this streaming from the edge the tension of the plane composite surface falls, and as it does so the extended lens contracts. The sheet formed by the first rapid extension of the lens of A frequently is unstable and ruptures. Circular spaces appear which are occupied by a composite surface similar to the composite surface outside the lens. The chief features on which I would insist here are (1) the relatively gradual formation of the composite surface by increase in the mass of A per unit area until it is in tensile equilibrium with a convex lens of A, and (2) the fact that when a lens of A is extended to form a sheet, the sheet is unstable if its thickness fall below a certain quantity.

When the fluid A has a sensible vapour tension—such as benzene or

* 'Roy. Soc. Proc.,' 1911, B, vol. 84, p. 220; also 1912, A, vol. 86, p. 608.

toluene—other features appear. Let us start with excess benzene placed on water, and exposed to air, the benzene is pulled out into an irregular sheet. When the air space is covered in so that it may become saturated with benzene vapour the sheet contracts to one or more lenses which are highly convex and quite immobile. These lenses are in tensile equilibrium with a composite surface of benzene and water. If the cover to the space be removed benzene evaporates from the composite surface, the tension rises, and the convex lens (or lenses) is at once pulled out to a sheet. It is very easy again to notice that an over extended sheet of benzene is unstable and ruptures. It will be noticed that whatever the vapour tension of A, whether it be high or insensible, the system settles down to the same state, namely, a composite sheet in tensile equilibrium with a convex lens of A. Now the tension of one face of the lens is T_{AB} , and of the other is T_A , or if B be soluble in A some quantity slightly greater than T_A . Therefore, since the lenses are convex we have for the equilibrium state the important relation $T_s < T_A + T_{AB}$.

In the case of the chemically saturated substances in Table I the lens is not pulled out to form a sheet, and fluid cannot be drawn from its edge on to the surface of the water since $T_A + T_{AB} > T_B$. But the vapour condenses on to the water since $T_{AB} < T_B$. This may readily be proved by pouring the vapour of octane, or carbon bisulphide, etc., on to a clean surface of water and noticing the movement of lycopodium grains dusted on to the surface.

When A is not a pure substance but a mixture of substances which individually produce effects of different magnitude upon the tension of B, the phenomena of spreading are more complex. Mixtures of *e.g.* cyclohexane or oil "C" and oleic acid or stearic acid at first flash over the surface as a continuous sheet which, viewed at certain angles, is uniformly and brilliantly coloured. From the particular colour we may put this sheet as from 300 to 1000 $\mu\mu$ thick. The sheet is unstable and ruptures, circular spaces appearing. As these spaces extend a horizontal net is formed, and finally the bars of the net rupture and the isolated masses contract to lenses. The total time occupied in forming the lenses, and the relative duration of particular stages depend upon the ratio of the components of A, upon their nature, and upon the concentration of electrolytes in the water. Increasing the number of components as a rule lengthens the total time and the complexity of the phenomena, and the vivid play of Newtonian colours is then very beautiful. By increasing the number of components a composite sheet may be formed of films of different thicknesses which pass abruptly into each other. The whole surface shows sharply determined coloured areas, red, blue, green, bronze, etc., which endure for days.

The phenomena ultimately depend upon the accumulation by diffusion of the most active constituents at the interface, and their complexity and durability are due to the slowness with which tangential diffusion can occur owing to the small depth of the film. The phenomena, occurring as they do on the surface of water, may be said to take place in two dimensions. If they occupied the mass of the fluid, that is to say, if they were in three dimensions, the unstable sponges, films, and lenses would yield the phenomena of the colloidal state, and especially of gelation. The horizontal networks which appear, and which are in an unstable state so far as surface energy is concerned, must represent in a crude way the mechanism of a muscle reduced to two dimensions, for there can be little doubt now that the force of muscular contraction is derived from changes in the energy of surfaces in the interior of each muscle fibre.

Curves of the change of tension produced by the spreading of A upon water, obtained by Wilhelmj's method of measuring surface tension, were given in an earlier paper (*loc. cit.*) and it was noticed that, when disturbance due to hysteresis of the surface is avoided, the curve for certain substances consists of a series of straight lines. I add here the curve for pure oleic acid (fig. 1). The vapour pressure is so low as to render the error due to

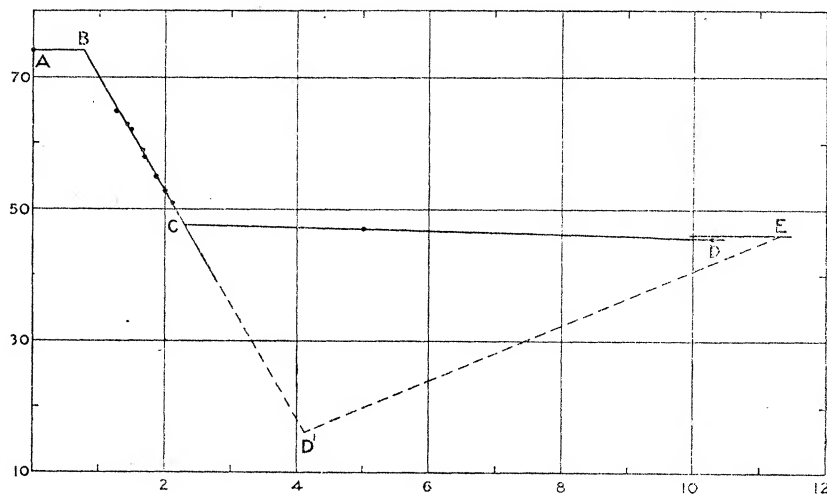


FIG. 1.

vaporisation from the surface negligible, but, unfortunately, the acid leaks past the barriers used to contract the film by diffusion through the body of the water, so that the observed tension tends always to be too high. In time, the oleic acid completely escapes from the control of the barriers, thus a contracted surface of tension 46.2 was left overnight, two barriers close

together confining it. Twenty hours later the tension had risen to 60.9. By again sweeping as much of the acid as possible on to the same restricted area the tension fell to 47.6 at the point marked with a cross in fig. 2. The curve for oleic acid is again the same type of curve—straight lines and sharp inflections. In the previous paper other curves are given in which there is only one sharp inflection and no part beyond this forms a

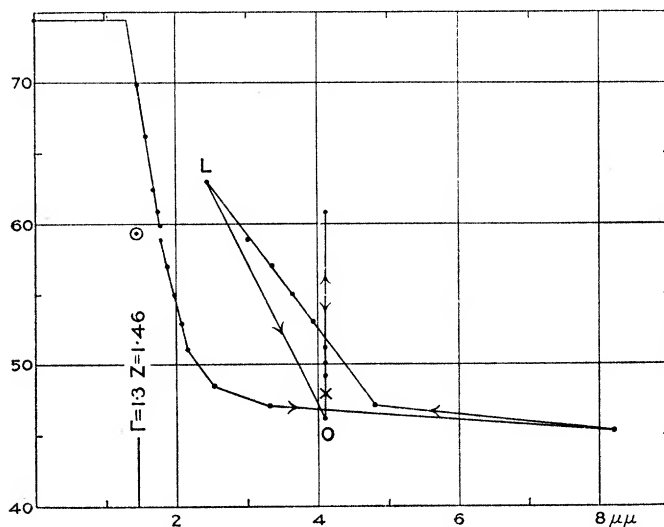


FIG. 2.

straight line. With the fuller knowledge now in my possession I regard such curves as characteristic of films composed of two substances at least, one having an effect on the tension of the surface less than that of the other.*

Measurements of the tension T_{AB} throw some light upon the singular features of these curves. Let it first be supposed possible by avoiding the formation of a lens (as *e.g.* by allowing vapour to condense on to the surface in the absence of nuclei) continuously to increase the mass of A per unit of surface area, a point will be reached when an independent surface of pure A is formed. The curve therefore begins at $T_s = T_B$ and ends at $T_s = T_A + T_{AB}$, both points being determinable by experiment. Of the intervening curve the first portion AB is horizontal or slightly undulating.† Lord Rayleigh interpreted it to be the region in which the quantity of A placed on the surface is insufficient to form a continuous

* The sample of cymene used previously was found to contain a small percentage of an impurity with a high boiling point.

† 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 623.

sheet. The objection to this interpretation is the dimensions of the molecule which follow from experiment. Taking, for instance, pure oleic acid, the depth of the film of acid at the point B is of the order 13×10^{-8} cm. Putting 10^{-8} as the diameter of the hydrogen atom, a molecule of the acid regarded as a sphere would have by the Barlow-Pope theory a diameter of only 4.8×10^{-8} cm. Perhaps a way out of the difficulty may be found ultimately by treating the point B as a critical point in the electric polarisation of the surface, also the calculated thickness of the film of A may be largely in excess of the real thickness, for complete immiscibility of A and B cannot be postulated, and some loss must occur owing to diffusion into the mass of B.

Lord Rayleigh remarks that "an essentially different result would seem to require a repulsive force between the molecules (of oil), resisting" contraction of the film. There is, as I have already pointed out, evidence to show that the oil spread on the surface is at a different electrical potential to the water. A repulsion due to the charge on each molecule of oil must therefore exist. But this only increases the difficulty, since such a tangential repulsion would, if it operated alone, bring about a fall in the tension before a continuous layer of oil was formed on the surface. It is open to us to suppose that one of the first effects of the oil is to undo a state of affairs at the surface of the water, namely, an average orientation of the water molecules themselves under the influence of the inwardly directed force of attraction, and thereby to increase the tension of the water, but a hypothesis which goes so far beyond ascertained fact cannot be so satisfactory as the direct explanation offered by Lord Rayleigh.

The significance of the inflection at C (fig. 1) is, I think, clear. It is the point where the continuous uniform sheet of A spread on B ceases to be stable and any further added quantity gathers into a lens. This occurs when the tension of the composite plane surface is equal to $T_A + T_{AB}$. The following table confirms this conclusion. T_C is the tension at the point C, as measured by Wilhelmj's method.

Castor oil.....	$T_C = 58.0$	$T_A + T_{AB} = 58.27$
Oleic acid	$= 47.5$	$= 46.30$
Ricinolic acid	$= 48.8$	$= 48.34$
" "	$= 45.0$	
Ethyl hydrocinnamate	(between 55.64 and 58.16^*)	$= 57.73$
Benzene	$= +64.0^\dagger$	$= 65.4$

* Camphor is still active on a surface on which a lens of this ester is standing, the space above being saturated with the vapour. Rayleigh fixes the camphor point at 57.7 .

† In order to maintain the surface against loss by evaporation it is necessary to have a flat lens of benzene, therefore Kg has a sensible value, and the tension observed is slightly lower than T_C .

The slope of the line CD is determined partly by the form of the lens or lenses on the surface, that is to say, by the quantities T_A , T_{AB} , and the density

of the fluid A or D_A ; and partly by the circumstance that the abscissæ are calculated from the total mass of A placed on the surface divided by the area. They do not, therefore, any longer represent the true mass of A per unit area of the composite surface, but an average of that quantity and the mass absorbed into the lens. Since this is always greater than the true value, the line CD should slope more steeply than it does in the figure. The point C, therefore, is not the lowest point of the curve. This conclusion follows from other considerations. In the case of chemically saturated substances C ($= T_A + T_{AB}$) lies on or above the level of T_B . In spite of this, vapour of any of these substances condenses on to a surface of pure water and in so doing lowers the tension. Also, as we have already seen, the relation $T_S < T_A + T_{AB}$ holds for all surfaces in which excess of A forms a convex lens on a composite surface of A and B, and such lenses are formed by the condensation of the vapour of carbon tetrachloride, benzene, etc., on to the surface of water. Lastly, the mechanical stability of a film formed from the composite surface is not minimal at C but at a point of lower tension produced by still further concentration of A on to the surface.* The true curve of the variation of tension of the composite surface of A and B, therefore, must fall below the point C to a minimum at D' and from C to D' the surface when realised is unstable with respect to lens formation. This explains an otherwise anomalous result which I have thrice obtained with exceedingly pure oleic acid spread on to a very clean surface of tap water (temperatures 14.5° and 11.5°), namely that at a certain point further thickening of the film of acid by contraction of the surface caused a sharp rise of tension which thenceforward remained constant at the higher level even when the film of acid was thickened as much as possible by extreme contraction of the surface. Each step in the contraction now gave rise to a sharp rise of tension, which at once gave way, the tension falling to the constant figure. Inspection of the surface with a hand lens left no room for doubt as to the explanation of the phenomenon, for it was seen to be covered by a dew of very tiny lenses. On extending the surface the dew disappeared just as though the acid had evaporated and the tension now rose and fell normally with movement of the barrier. On again contracting the surface the dew reappeared and the tension at once became practically independent of the area. It is probably not owing merely to accident that this striking phenomenon of supersaturation has been observed only when a substance of high chemical purity was used.

At D' some new physical factor must come into operation. One supposition open to us is that at D' the attraction of B for A is fully

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 630.

satisfied. This would make Γ_D/D_A equal to the range of the attractive force between the fluids B and A if the density of A on the composite surface be put equal to that of A in mass. Γ is the mass of A per unit area of surface.

The part of the curve D'E, of unknown slope, would then relate entirely to the work expended in forming a layer of a new phase, namely pure A, and the process is complete at E when the tension of the upper face becomes T_A , and that of both faces $T_A + T_{AB}$. The two tensions are now equal to the tension at C, which, however, is that of a single true composite surface.

The diagram (fig. 3) may serve to make the explanation clearer. On it are shown curves for four substances, the point D' being in each case put equal to T_{AB} . The scale of the abscissæ and the slope of the lines is entirely arbitrary. At the point C on each curve the tension of the composite surface has fallen to the equality $T_s = T_A + T_{AB}$, save in the case of the chemically saturated substance, when T_s is always $> T_A + T_{AB}$. From C to D' the composite surface is stable with respect to infinitesimal variations of the mass of A per unit area, but unstable with respect to finite variations. That is to say, a lens cannot form spontaneously, because any tendency to a local accumulation of the fluid A will be resisted by the tension of the surface. But if suitable nuclei are present, or if a lens of A be placed on the surface, condensation must occur. If the curve from B to D' be a straight line we have, as the equations of this part,

$$\frac{dT_s}{d\Gamma} = -c \quad (1) \quad \text{and} \quad T_s = C - c\Gamma, \quad (2)$$

Γ being the mass of A per unit area of surface.

The part D'E is a region of complete instability, hence, as has already been pointed out, when a lens of A is extended to form a sheet, the sheet ruptures when its depth is diminished below a certain minimum. The form and slope of this part are entirely unknown.

The changes of the vapour pressure of A in equilibrium with the composite surface cannot be followed with any certainty, though something may be said about them. At A on the curve the vapour pressure of the fluid A

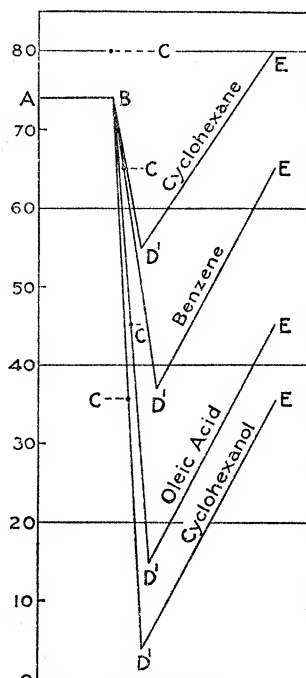


FIG. 3.

in a closed space above the surface would of course be zero, and at E it is that of the vapour saturated in contact with pure A in mass. Between these points we have the relation established by Gibbs,* namely

$$dT_s = -\frac{\Gamma}{\gamma} dp, \quad (3)$$

in which Γ is the excess of A concentrated on unit area of the surface over what would be there if no concentration occurred. Γ therefore has sensibly the same significance as that given to it in this paper; γ is the density of the vapour. As an approximation we may put $\gamma = p/R\theta$, in which R is the gas constant, and θ the absolute temperature on the thermodynamic scale. Equation (3) now becomes

$$dT_s = -\Gamma R \theta \frac{dp}{p},$$

which for limits Γ_0 and Γ_1 , when the vapour is compressed isothermally on to the surface, becomes

$$(T_1 - T_0) = -R\theta \int_{\Gamma_0}^{\Gamma_1} \frac{\Gamma}{p} \frac{dp}{d\Gamma} d\Gamma,$$

an equation which can be integrated only if we know the form of the function $dp/d\Gamma$.

Equations connecting the vapour pressure with the tension of the composite surface are given by Warburg† and Cantor,‡ but they cannot be trusted owing to faulty reasoning. In both cases they are derived by equating the balance of work gained to the change in the potential of the surface when fluid is evaporated from A and condensed on to the surface of B, the series of operations performed upon A being essentially those used by Helmholtz§ in his calculation of the change of free energy when a quantity dm of water is evaporated from the plane surface of a mass of pure water, and condensed into a solution of salt in water. In the final process, when the water vapour is condensed into the salt solution, Helmholtz puts the pressure constant, and the work therefore simply equal to pv . This is correct only if the mass of the salt solution be infinite. Warburg and Cantor follow the procedure of Helmholtz in that they put the pressure of the vapour of A constant while it is being condensed on to the surface of B. This is equivalent to putting T_s constant throughout the operation, and is obviously wrong.

Something may be said in answer to two questions, namely, (1) at what

* 'Trans. Conn. Acad.,' 1878, vol. 3, p. 398.

† 'Ann. Physik u. Chem.,' 1886, vol. 28, p. 394.

‡ *Ibid.*, 1895, vol. 56, p. 492.

§ 'Mem. Phys. Soc.,' vol. 1, Part II.

point on the curve is the vapour pressure of A maximal? and (2) at what point is it equal to that of the vapour tension of pure A?

Equation (3) may be written

$$\frac{dT_s}{d\Gamma} = -\frac{\Gamma}{\gamma} \frac{dp}{d\Gamma}.$$

Since Γ/γ is necessarily positive the curve would begin to ascend when $dp/d\Gamma$ becomes negative—that is, when for any further addition of A to the surface its vapour pressure falls. This would happen along D'E; and the fall in vapour pressure would be strictly analogous to that which occurs when spheres of fluid in equilibrium with vapour about them fuse to form a larger sphere or a plane sheet. At D', therefore, the vapour pressure of A would be maximal. It would also be supersaturated with reference to a plane surface of A, since along D'E it is falling to the pressure of saturated vapour at E.

Passing backwards from D' towards C the vapour tension of A at the composite surface is at first greater than the vapour pressure of pure A, and the surface would be in both tensile and vapour equilibrium with a convex lens of A. At some point the tension of the vapour at the composite surface falls to an equality with that of a plane surface of pure A. The point at which this happens will depend upon the pressure of the saturated vapour and, since T_{AB} changes only slowly with temperature, the point would fall lower and lower on the line CE' as the temperature rises. That this is so appears from measurements made by Clark* of the tension at the interface of ethyl ether and glycerine, and of a surface of glycerine in contact with a vapour space in which the vapour was maintained in equilibrium with the pure ether. The quantity T_s is always $> T_{AB}$ except near the critical point of ether, when it is $< T_{AB}$. It is interesting that in both cases the curves which connect temperature and T_s and T_{AB} respectively are sensibly straight lines. The curve for T_s is at ordinary temperature high above that of T_{AB} but, falling more rapidly, it cuts the latter at about 170°—the critical temperature of ethyl ether being 194°.

The way in which vapour is as it were flung off a surface during spreading points very decisively to a large rise in the tension of the vapour of A at some stage in the process. Ethyl hydrocinnamate boils at 247—249° according to Beilstein, and as it is immiscible with water I hoped this ester would serve for measurements of the change of tension produced by thin films spread on water. It proved, however, to be quite impossible to obtain any measurements owing to the fact that quite large quantities of the ester

* 'Proc. Amer. Acad. of Arts and Sciences,' 1906, vol. 41, p. 361.

evaporate practically completely from the clean surface of water in less than a minute. The evaporation is accompanied by violent currents and eddies on the surface. Measurements of the tension prove that evaporation is not from the fully extended sheet of ester, for, though the excess of each drop placed on to the surface evaporates, a residue remains as a film which causes a permanent fall of tension. Also, when the sheet of ester has been sufficiently thickened by a succession of drops (the larger part of each being lost by violent evaporation) and in that way the tension lowered permanently to ± 56 dynes, the rapid loss of vapour ceases and a thin extended sheet of ester will lie quietly upon the surface. It would occupy too much space to describe the complicated changes which occur when a lens of this ester is trying to spread over a surface of high tension, but, taken together, they show that the expulsion of vapour occurs only near the edge of an extended lens. Consider what happens when a lens is extended by a higher tension. In the processes of expansion and thinning of the sheet it must be dragged through the whole region of instability and high vapour pressure from E through D' to C. The only way of escape is for the unstable sheet to gather into small lenses, and this is what continually happens, very small lenses being formed by and cast off from the edge of the main sheet. The result in the main is that the potential energy of a lens of ester standing on a surface of high tension is partly expended in boiling the ester off the surface.

Any explanation of the variation of tension with the varying depth of the film of A to be adequate must include an explanation of the remarkable movements of *e.g.* a pair of lenses of carbon bisulphide on a clean water surface. To exhibit the movements to perfection the lenses must be small and highly convex. If they come within about 1 or 2 cm. of each other they are violently attracted and move directly towards each other until the edges are nearly in contact, when equally violent repulsion occurs. In this way rapid alternate attraction and repulsion occurs, always, if undisturbed, accurately along a line joining the centres.

The explanation is I think as follows:—Consider each lens when out of the sphere of influence of the other. Vapour is being condensed on to the water face to form a film which spreads as a film centrifugally until it is destroyed by evaporation. The lens is thus the centre of an area of lowered tension, which therefore forms a depression. When two lenses come sufficiently close together these depressed areas fuse and a trough is formed between the centres along which they move—the trough deepening as they approach.

With the near approach of the lenses the vapour sheet is thickened until

the tension falls to D' , beyond this there would be an abrupt rise of tension and a repulsion. The obstacle to the fusion of the lenses which is so obvious is the portion $D'E$ of the curve and a pair of lenses must acquire a critical quantity of kinetic energy before they can break through it.

A relation found by Antonoff from measurements of interfacial tensions would, when it holds, fix the vapour pressure of the fluid A at the point C on the curve as very near to that of a saturated solution of A in B. Using partially miscible substances, Antonoff* finds that the interfacial tension is equal to the difference between the tensions of the two phases. That is, in our notation,

$$T_{ab} = T_b - T_a, \quad (4)$$

and at the limit when the fluids are immiscible

$$T_{AB} = T_B - T_A.$$

Clearly the relation is not universal, nor even a very common one, for, taking fluids sensibly immiscible with water, we have

Table II.

	$T_B - T_A$.	T_{AB} .		$T_B - T_A$.	T_{AB} .
Cyclohexane.....	50.0	55	Carbon tetrachloride...	50.0	50
Octane	53.4	53	Castor oil	38.7	23
Oil "C"	44.0	61	Ethyl cinnamate	37.0	24
Carbon bisulphide ...	43.0	56	Ethyl hydrocinnamate	40.5	24

It will be noted that cyclohexane, oil "C," and carbon bisulphide are exceptions to Quincke's rule that T_{AB} is always less than $T_B - T_A$.

I am at a loss how to criticise Antonoff's values, since they purport to be calculated by the erroneous equation $T_s = m/2\pi r$. This would give results 40 to 50 per cent. wrong, but his figures agree with mine in the very low value for the quantity T_{AB} for alcohols, and in the value found for benzene. The values for T'_{AB} calculated from his figures also agree with those found by me for alcohols.

	T_{AB} .	T'_{AB} .
Isoamyl alcohol	4.43	44.59
Isobutyric alcohol	1.76	46.75
Benzene	32.6	34.2

It is possible that though the faulty equation is quoted with approval, the experimental results were obtained with tubes standardised by measuring the tension of some pure fluid whose tension is known.

The explanation of Antonoff's relation is simple, and its theoretical significance not great. If water is saturated with a fluid which causes the tension of water (T_B) to fall, the surface will also become saturated with this fluid. When this happens T_B is reduced to the tension at C on the curve,

* 'Journ. de Chim. Physique,' 1907, vol. 5, p. 372.

which, as we have already seen, is that of a surface saturated with A and is equal to $T_A + T_{AB}$. We therefore have $T_b = T_A + T_{AB}$, and equation (4) now becomes

$$T_{ab} = T_A + T_{AB} - T_a,$$

which, since T_a is always sensibly equal to T_A , means that T_{ab} is sensibly equal to T_{AB} , and this has already been found to be the case.

The portion of the curve BD in the diagrams is drawn as a straight line for reasons which are given in an earlier paper. The curves which Lord Rayleigh gives of the changes of tension with variation in the thickness of a film are gradually bending lines,* and from theoretical considerations he concludes that the tension of a composite surface of A spread on B should vary as the square of the thickness of the film of A.† The question, in the long run, must be decided by experiment, and I therefore add a table of constants (Table III) calculated from measurements of tension by Wilhelmj's method, the thickness of the film of A being varied by contracting the surface with movable barriers.

The method of thickening a film by sweeping it up on to a contracted area by blades is open to many objections. Though leakage of the surface past the barriers may be avoided, loss by diffusion must occur to some extent, since perfect immiscibility cannot be postulated. A contracted film of pure oleic acid in 20 hours had again distributed itself evenly over the entire surface, largely, so far as I could determine, by diffusion through the body of the water. There is thus always a decrement which tends to make the curve bend away from the axis of tension. The result of many measurements is to show that the more accurately and rapidly the series of measurements are made the more closely does the curve approximate to a straight line.

The most successful series I was able to obtain with oleic acid is plotted in fig. 4, and the constants are given in the third column of Table III. Three barriers were used to contain the film and, as far as possible, kept touching each other throughout. The water used was carefully cleaned tap water. The readings were taken rapidly and were very steady until the first inflection of the curve at M; here, owing to some unknown cause, leakage occurred, the tension rising while the weight was being recorded. At N the tension rose abruptly to O owing to the formation of exceedingly fine lenses, each of which appeared under a hand lens as little more than a point. A further slow rise from O to P occurred in nine minutes, and during this nine minutes some lycopodium dust drifted 2.5 cm. away from the barriers on the side

* 'Phil. Mag.,' 1899, [5], vol. 48, p. 331.

† *Ibid.*, 1892, vol. 33, p. 468.

remote from the contracted film of oleic acid. The rise OP therefore was due to a very slow leakage past the barriers.

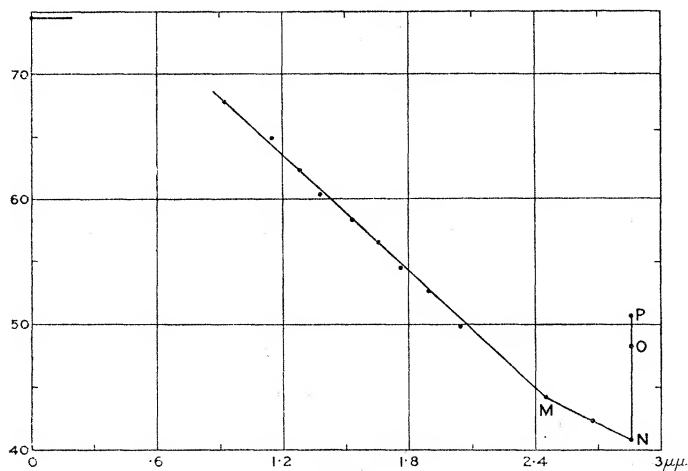


FIG. 4.

Table III.

Ts.	C _i .	C _{ii} .	C _{iii} .	C _{iv} .
72.4	23528			
71.8	26188			
70.85	25612			
69.9	27892			
68.9	28652			
67.8	—	—	15.658	
67.0	27450			
66.0	—	—	—	15238
65.4	—	—	—	15036
64.9	—	—	15.127	
63.9	—	—	—	15070
63.5	—	—	—	15316
63.0	26503			
62.5	—	—	15.562	
62.0	—	17390	—	15180
60.4	—	—	15.830	15198
59.0	26831	18067	—	15252
58.5	—	—	15.523	
58.0				
57.0	20045			
56.5	—	18000	15.443	14960
55.0				
54.6	—	—	15.694	
53.0	—	17415		
52.6	—	—	15.587	
51.0	—	17405		
49.9	—	—	15.796	
44.25	—	—	15.486	
42.5	—	—	14.831	
40.9	—	—	14.457	

C_i, C_{ii}, C_{iii} refer to three separate measurements made with pure oleic acid. C_{iv} to castor oil. C_i, C_{ii}, C_{iv}, the constants are in arbitrary units. C_{iii}, the units are dynes per linear centimetre and 10⁻⁷ cm.

The particular form of the curve near the second inflection (at point C) depends upon the conditions which favour or hinder lens formation such as the number and nature of solid particles or other nuclei in the surface film, and is not of very great theoretical interest. Sometimes the inflection is remarkably sharp, at others it is gradual.

If the curve be a straight line, then we have

$$\frac{dT_S}{d\Gamma} = -c \quad \text{and} \quad T_S = C - c\Gamma,$$

C being the integration constant. This last equation may be written

$$T_S = T_B - c(\Gamma_S - \Gamma_0), \quad (5)$$

Γ_0 being the mass of A per unit area of surface at the point C in the curve.

The relation $dT_S/d\Gamma = \text{constant}$ is of considerable theoretical interest if it can be established, for let us consider a composite surface formed by removing a layer of depth Δ from A and applying it to B. Then if ΔT_A is the work expended per unit area in removing the layer from A to ∞ and $2\Delta T'_{AB}$ the work gained from the attraction of B for A in bringing it to rest on B we have

$$T_S = \Delta T_A + T_B - 2\Delta T'_{AB}.$$

Let ρ_A, ρ_B be respectively the density of the fluids A and B, then if $m\rho_A\psi_A(z)$ is the attraction between a mass m of A distant z from an infinite mass of A and the latter, the work needed to remove to infinity a sheet of thickness dz is, per unit area, $\rho_A^2 \int_z^\infty \psi_A(z) dz$.

Call this integral $\theta_A(z)$, then ΔT_A becomes equal to $\rho_A^2 \int_0^\Delta \theta_A(z) dz$.

Similarly, $2\Delta T'_{AB} = \rho_A \rho_B \int_0^\Delta \theta_{AB}(z) dz$,

and we have $T_S = T_B + \rho_A^2 \int_0^\Delta \theta_A(z) dz - \rho_A \rho_B \int_0^\Delta \theta_{AB}(z) dz$

and $\frac{dT_S}{dz} = \rho_A^2 \theta_A(z) - \rho_A \rho_B \theta_{AB}(z)$.

But $\Gamma = \Delta \rho_A$ and $d\Gamma = dz \rho_A$, (6)

therefore $\frac{dT_S}{d\Gamma} = \rho_A \theta_A(z) - \rho_B \theta_{AB}(z)$; (7)

and, since $\frac{dT_S}{d\Gamma}$ is by experiment equal to a constant,

$$\theta_A(z) = \frac{\rho_B}{\rho_A} \theta_{AB}(z) + \beta, \quad (8)$$

where β is another constant.

$\theta_A(z)$ is the function of the potential of A at the surface of A, and $\theta_{AB}(z)$ of A at the surface of B, hence we may conclude that if $dT_s/d\Gamma$ is equal to a constant the form of these functions must be the same.

We may perhaps proceed a stage further. Laplace assumed that the function of the attractive force between matter at minute distances is the same in all cases, "the attraction differing merely by coefficients analogous to densities in the theory of gravitation." On this assumption we may write equation (7)

$$\frac{dT}{d\Gamma} = \alpha\theta_A(z), \quad (9)$$

and $\theta_A(z)$ is then seen to be a constant, a result which is in agreement with the suggestion of Young that molecular attraction is a force which is constant in magnitude over the very minute range through which it acts. But the range in question must be less even than the thickness of the films of oil which when spread upon water reduce the tension, for, if $\theta(z)$ be constant, then since $d\theta(z) = -\psi(z)$ this last function is equal to 0. The physical significance of this last relation would be that each layer of molecules of A spread on the surface is attracted only by the layer of molecules previously there with which it comes into contact, a result not inconsistent with many aspects of this difficult question but altogether inconsistent with the view that the attraction of B for A ceases only at the point D' in the curve.

Though such conclusions, based as they are upon an assumption of uniform density throughout an interface, cannot have great value, they are interesting as pointing to an unexpected simplicity in molecular forces. The simple spatial relations which are the essence of the Barlow-Pope theory of the molecular structure of close-packed forms of matter also seems to demand some simple law. If there were, for instance, alternating zones of attraction and repulsion about each molecule, more than one arrangement in space would satisfy the condition of minimal potential, and it would be possible by adequate pressure to compress a fluid to a volume which it would continue to occupy when the pressure was lowered.

The unexpectedly simple relation $dT/d\Gamma = -a$ constant would appear to hold for an interface between solid and fluid. A large amount of work has shown that when a solute such as iodine is condensed on to the surface of, for instance, animal charcoal, the equilibrium reached is given by the empirical equation $m = Kc^{1/n}$, where m is the mass of the solute condensed on to the surface, c the final concentration of the solution, and k and n are parameters. Putting the area of the surface of the solid as unity, this may be written

$$\gamma = \alpha\Gamma^n,$$

which on differentiating gives

$$d\gamma/d\Gamma = an\Gamma^{n-1} = n\Gamma/\gamma.$$

By comparison with Gibbs' equation $\Gamma = -\frac{\gamma}{R\theta} \frac{dT}{d\gamma}$, we get

$$\frac{dT}{d\Gamma} = -nR\theta.$$

Hence for an isothermal change $dT/d\Gamma$ is a negative constant.

Another significance of the constant c in (5) must not be lost sight of. Comparing the relation $dT_s = -cd\Gamma$, with the similar equation for volume energy $(dP) = Kd\gamma$, in which γ is the mass in unit volume, we see that C corresponds to K which in the gas equation is the gas constant R . But, whereas R implicitly refers to a zero of temperature, namely, the absolute zero, the constant c is related to the temperature of complete miscibility of A and B when T_s is zero.

If the fields of force about a molecule are not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the centre of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random disposition which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must therefore have a characteristic molecular architecture, and the condition of minimal potential involves two terms, one relating to the variation in density, the other to the orientation of the fields of force.* When the composite surface is formed its architecture is determined by the interaction of the fields of force of molecules of A and B under the influence of the attraction of B for A. When the structure is complete the tension T_{AB} is reached and any further addition of molecules of A to the surface does not disturb the architecture. But, just as there are in many cases two arrangements of the same molecules in the solid state, that of the glass, and that of the crystal, the former containing the greater quantity of energy per unit of mass, so in the formation of these films of matter the architecture actually reached may not always be that of least potential.

Description of Figures.—Save for the diagram fig. 3 the scale of the ordinates is dynes per linear centimetre, that of the abscissæ 1×10^{-7} cm.

* Lord Rayleigh ('Phil. Mag.,' 1892, vol. 38, p. 309) has shown that the deviations from Fresnel's formula for the reflection of light at a liquid surface may be traced to the presence of a film of impurity on the surface. The residual deviation which persists when all such films are swept away may, perhaps, be attributed to the real surface film of the pure fluid.

($\mu\mu$), calculated from the weight of acid spread on the surface on the assumption that the density of the film is that of oleic acid in mass. Fig. 1 is plotted from a particular experiment with pure oleic acid—that is to say with the purest acid which Kahlbaum prepares, further purified by fractional crystallisation. The line BC has been followed by Miss Pockell's method into the unstable region CD', until the end of the continuous line. The horizontal line through E marks the tension which is equal to the sum of the tension of the pure acid and that of the interface between acid and water or $T_A + T_{AB}$. Fig. 2 illustrates a prolonged experiment with oleic acid. The curve is interrupted at one point where there was an accident to the balance, the result being to alter the slope of the curve. The curve was followed without pause, save for the accident just alluded to, to the point O, when the barriers were left in position. The tension rose in 10 minutes to the first dot, and 20 hours later it was found to be at the top of the vertical line. By again concentrating as much as possible of the oleic acid on to the same area the tension fell to the point marked with a thick cross. The contraction of the surface from L to O was made very rapidly. The ringed dot marks the tension when 0.1 mgrm. of oleic acid was spread on to a surface of clean distilled water 685.7 cm.² in extent. For this tension therefore $\Gamma = 1.3 \times 10^{-7}$ gram. and $z = 1.46 \mu\mu$. The scale of the abscissæ is based upon this measurement. The remaining figures are adequately explained in the text.

Appendix 1.—In a previous paper* I pointed out that the mechanical stability of a composite surface is maximal just beyond the point B in the curve when the tension begins to fall. The measure of mechanical stability was the time which elapsed between the formation and bursting of bubbles of a particular size on the surface. The rise in mechanical stability from zero to a maximum was found to occur at a point some distance lower on the curve than B. The reason for this displacement is simple. When a film is formed at the surface by allowing a bubble of air to ascend from below, the surface is stretched and the quantity Γ , that is the concentration of the fluid A spread upon the water, thereby diminished. The effect is to put the state of the surface backwards along the curve towards the inflection at B. If the film is sufficiently stretched, that is if the bubble is large enough to make $\Gamma < \Gamma_B$, the bubble at once bursts. The amount of displacement of the rise of mechanical stability forwards along the curve is thus a function of the radius of the bubble of air. With infinitely small bubbles it would coincide with the inflection at B, where theory would place it.

Appendix 2.—An attempt to measure the tension of a composite surface in

* 'Roy. Soc. Proc.,' 1912, A, vol. 86, p. 627.

equilibrium with the saturated vapour of cyclohexane failed and the failure is instructive. Let a large lens be formed on the surface of water in a closed space. When the vapour pressures are in equilibrium since the lens of cyclohexane is sensibly flat the vapour tension must be that of saturated vapour. In order to calculate the tension of the composite surface of water and condensed vapour of cyclohexane we have the relation

$$T_s = T_A + T_{AB} - \frac{1}{2}g(D_A h^2 - D_A h'^2 + D_B h'^2)$$

and the hydrostatic equation

$$D_A h = (D_B - D_A) h'.$$

h and h' refer respectively to the height of the upper surface of the lens above the surface of the water and the depth of the lower surface below it; h and h' very approximately can be got by measuring the area of the lens and its volume, and taking the thickness as uniform.

I found that when placed on tap water of tension 73.6, the vapour space being small, 0.5 c.c. cyclohexane formed a lens 6.4 cm. in horizontal diameter, 2 c.c. a lens 13.5 cm. diameter. The last term is negligible for lenses so thin (0.015 cm. and 0.014 cm. respectively), and T_s calculated is 79.34 and 79.35. Clearly, therefore, T_{AB} must have been reduced by the accumulation at the interface of some trace of impurity. The changes observed agree with this, for the cyclohexane when first put on forms a convex lens which slowly flattens out. The flattening cannot be due to an increase in T_s above T_B since the condensed vapour lowers the tension, as is readily seen by admitting a little air so as to relieve the concentration of the vapour of A, when the flattened lens at once contracts.

Appendix 3.—The arguments employed in this paper throw light upon a suggestion put forward by Laplace, and incidentally on that vexed point the physical significance to be attributed to the term “density” as used by Laplace. By the Young–Laplace theory we have for the intrinsic pressure and the surface tension of a fluid respectively

$$\kappa = 2\pi\rho_2 \int_0^\infty \psi(z) dz \quad (10) \quad \text{and} \quad T = 2\pi\rho_2 \int_0^\infty z\psi(z) dz. \quad (11)$$

Laplace assumes that $\psi(z)$, like gravity, is a function depending only on the density of the substance, and we may therefore write

$$T = \rho^2 T_0 \quad (12) \quad \text{and} \quad T'_{AB} = \rho_A \rho_B T_0. \quad (13)$$

From (10) and (12) follows

$$T_{AB} = (\rho_A - \rho_B)^2 T_0.$$

It has been objected that the facts do not accord with this relation. This

is true, but the cause may lie either in the fact that T_0 is constant only for similar fluids—that is for fluids of the same chemical type, or in the difficulty in identifying the density of Laplace's theory with a particular physical property.

Comparing equations (3) of the paper preceding and (12) we get

$$\rho_0^2 T_0 = \frac{(\tau - d)}{\nu^{2/3}} \kappa.$$

If the density be taken as a molecular quantity then $\rho = 1/v$ and $T_0 = (\tau - d) \kappa V^{-1/3}$. From this we can derive equation (4) of the preceding paper as the expression for the interfacial tension.

The expression $T_{AB} = (\rho_A - \rho_B)^2 T_0$ is now seen to be wrongly derived, the false assumptions being the identity of κ_A with κ_B , and of $(\tau_A - d)$ with $(\tau_B - d)$. And for a similar reason the expression $T'_{AB} = \rho_A \rho_B T_0$ is inadmissible.

A Simple Method of Finding the Approximate Period of Stable Systems.

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In practical engineering work it is often a great convenience to be able to find the period of a structure, the calculation of which, by ordinary mathematical processes, would be difficult or even impossible. To find the period of a structure for any particular mode of vibration involves a knowledge of its stiffness (regarded as a spring) and of the distribution of the mass, but if the latter is known, even approximately, a knowledge of the period gives the stiffness, and the deflections for a given load can be found by simple arithmetic.

In nearly every case likely to occur in practice a stable structure can be represented, as far as its elastic displacements are concerned, by an equivalent pendulum, a pendulum, that is, which has the same period as the particular mode of vibration under consideration, and an effective mass equal to that part of the mass of the structure which is subject to vibration, but concentrated at what, for the present purpose, may be called the centre of oscillation.

The proposition on which the simple determination of period above referred to depends is as follows:—